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The first conglomerate in fluorinated asymmetric nitrogen compounds[†]

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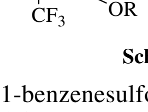
Based on X-ray diffraction analysis, it was found that 1-*p*-toluenesulfonyloxy-2,2-bis(trifluoromethyl)aziridine crystallises as a true racemate, whereas 1-benzenesulfonyloxy-2,2-bis(trifluoromethyl)aziridine forms a conglomerate.

Fluorinated aziridines are of importance in the chemistry of three-coordinated asymmetric nitrogen. Hexafluoroacetone oxime, which was synthesised for the first time by Knunyants *et al.*[2] in 1963, was used for the preparation of O-substituted 1-hydroxy-2,2-bis(trifluoromethyl)aziridines.[3] Next, aziridine **A**, as well as configurationally, chemically, and thermally stable compounds **1**, **B**–**D** (Scheme 1), were isolated in optically active forms with the use of chiral resolving reagents, and their absolute configurations were determined.[3(h)]



1 R = Ts[3(a),(d)]
A R = H[3(a),(b)]
B R = CO_2Alk[3(c),(d)]
C R = CH_2CO_2H[3(f)–(h)]
D R = CMe_2CO_2H[3(e),(g),(h)]

Scheme 1

Previously, 1-benzenesulfonyloxy-2,2-bis(trifluoromethyl)-aziridine **2** and its 2-monomethyl analogues (**E**, **F**)[3(d)] were synthesised and studied.

Based on the kinetics of the *cis*–*trans* isomerisation **E** → **F** (Scheme 2), the very high barrier of inversion $\Delta G^{\#} = 30$ kcal mol^{-1} at 120 °C was found.[3(d)] Aziridine **1** was obtained as optically

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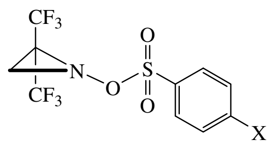
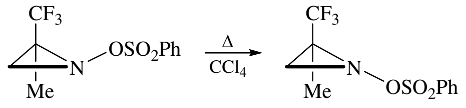
[†] Asymmetric Nitrogen, Part 97. Part 96 see ref. 1.

[‡] **1**: mp 66–67 °C (*n*-hexane–diethyl ether). **2**: mp 43–44 °C (*n*-hexane–diethyl ether). NMR spectra see in refs. 3(*b*),(*e*).



1 X = Me
2 X = H



E **F**

Scheme 2

active species.[3(a)] However, the not very great difference between the melting points of compounds (±)-**1** and (+)-**1** or (–)-**1** ΔT_{m} = 12–14 °C[3(a)] cannot be unambiguous evidence for the hetero- or homochiral crystallization of (±)-**1**, whereas aziridine **2** in an optically active form was not obtained at all.

In this work, in order to find conglomerates, we synthesised aziridines **1** and **2**[‡] and studied their crystal structures.[§]

According to X-ray diffraction analysis, compound **1** crystallises in the centrosymmetric space group $P\bar{1}$ while **2** in the chiral space group $P2_12_12_1$. The comparison of bond lengths and angles in **1** and **2** revealed that they are practically identical (Figures 1 and 2). The N(1) atom is significantly pyramidalised: the deviation of the N(1) atom from the plane of the C(1), C(2) and O(1) atoms is equal to 0.76 or 0.74 in **1** or **2**, respectively. The only difference between **1** and **2** is observed for mutual disposition of PhSO$_2$O and aziridine moieties. In **1**, the tosyl is located in front of the bis(trifluromethyl) fragment whilst in **2** the Ph group is synclinal to the above fragment [the pseudo-torsion angle C(1)N(1)S(1)C(5) is equal to 55.1 or 157.7° in **1** or **2**, respectively]. It should be noted that mutual dispositions of CF$_3$ groups with respect to the aziridine ring as well as Ph plane in respect to the O(1)S(1)O(2) one in molecules studied are almost identical.

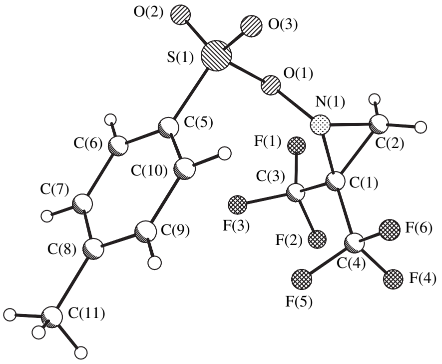


Figure 1 General view of **1**. Selected bond lengths (Å): S(1)–O(1) 1.632(1), O(1)–N(1) 1.456(2), N(1)–C(1) 1.489(2), N(1)–C(2) 1.467(2), C(1)–C(2) 1.480(2); selected bond angles (°): O(1)–S(1)–C(5) 103.85(7), S(1)–O(1)–N(1) 108.99(9), O(1)–N(1)–C(2) 108.7(1), O(1)–N(1)–C(1) 109.5(1), C(2)–N(1)–C(1) 60.1(1).

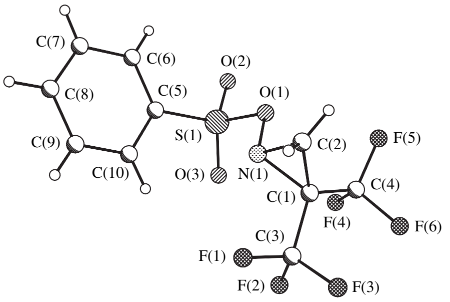


Figure 2 General view of **2**. Selected bond lengths (Å): S(1)–O(1) 1.6276(5), O(1)–N(1) 1.4605(8), N(1)–C(1) 1.489(1), N(1)–C(2) 1.470(1), C(1)–C(2) 1.491(1); selected bond angles (°): O(1)–S(1)–C(5) 104.50(3), S(1)–O(1)–N(1) 108.24(4), O(1)–N(1)–C(2) 109.66(6), O(1)–N(1)–C(1) 112.07(5), C(2)–N(1)–C(1) 60.51(5).

The above variation of the mutual disposition of the aromatic ring in respect to bis(trifluromethyl) fragment, in turn, leads to the in principal different crystal packings in **1** and **2**. Although the methyl group in tosyl does not participate in any shortened contact, its introduction is sufficient to change the nature (F···F, O···H, F···π) and number of intermolecular contacts and, as a consequence, the chirality of the crystal.

It should be noted that, although **2** crystallises in the chiral space group, the determination of the absolute configuration by means of Flack's parameter has shown that **2** is a racemic twin. Analogous conclusions were also obtained with the use of polarimetric analysis.

Thus, we found that compound **1** crystallises as a true racemate, whereas compound **2** as a conglomerate. Note that in the aziridine series, only two spontaneously resolvable conglomerates are currently known.[4]

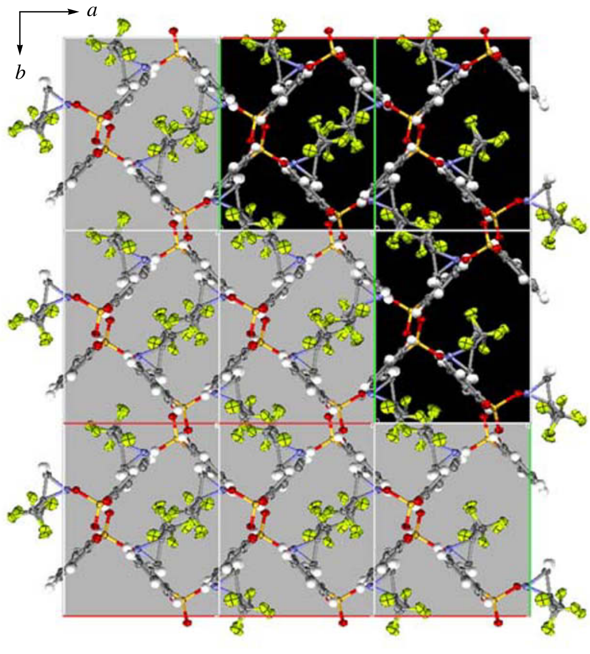


Figure 3 The probable way of laminar epitaxy in **2**. The fragments with opposite chirality are shown by black or grey.

[§] *Crystallographic data for compounds* **1** *and* **2**. The crystal of **1** ($C_{11}H_9F_6NO_3S$) is triclinic at 178 K, space group $P\bar{1}$, $a = 7.9295(16)$, $b = 9.607(2)$ and $c = 9.657(2)$ Å, $\alpha = 104.55(3)°$, $\beta = 98.35(3)°$, $\gamma = 99.36(3)°$, $V = 689.1(3)$ Å^3, $Z = 2$ ($Z' = 1$), $M = 349.25$, $d_{\mathrm{calc}} = 1.683$ g cm^{-3}, μ(MoKα) = 3.16 cm^{-1}, $F(000) = 352$; the crystal of **2** ($C_{10}H_7F_6NO_3S$) is orthorhombic at 120 K, space group $P2_12_12_1$, $a = 9.1596(2)$, $b = 11.3975(3)$ and $c = 12.2331(3)$ Å, $V = 1277.09(5)$ Å^3, $Z = 4$ ($Z' = 1$), $M = 335.23$, $d_{\mathrm{calc}} = 1.744$ g cm^{-3}, μ(MoKα) = 3.37 cm^{-1}, $F(000) = 672$.

Intensities of 5100 (**1**) reflections were measured with Syntex $P2_1$ [λ(MoKα) = 0.71072 Å, $\theta/2\theta$ scan, $2\theta < 64°$] at 178 K and the intensities of 43354 reflections (**2**) were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scan, $2\theta < 100°$] at 120 K and 4797 (**1**) and 12915 (**2**) independent reflections were used in further refinement. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms were located from the Fourier density synthesis. The refinement converged to $wR_2 = 0.1107$ and GOF = 0.981 for all independent reflections [$R_1 = 0.0422$ was calculated against F for 2696 observed reflections with $I > 2\sigma(I)$] for **1**; to $wR_2 = 0.0698$ and GOF = 1.002 for all independent reflections [$R_1 = 0.0340$ was calculated against F for 9366 observed reflections with $I > 2\sigma(I)$] for **2**. All calculations were performed using SHELXTL PLUS 5.0.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 610120 and 610121. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

The spontaneous resolution of compound **2** gives the basis for the simple preparation of optically active aziridines, which are shown in Scheme 1, and for the determination of the mechanism of the dual reactivity of compounds **1** and **2** towards nucleophiles.[3(c)]

The racemic twinning observed in the crystals of **2** is a widespread obstacle for spontaneous resolution; usually, it is due to the alternation of layers composed of various enantiomers.[5] Based on an analysis of crystal packing, it is believed that laminar epitaxy also occurs in compound **2** (*cf*. ref. 5) in the crystallographic plane (110) (Figure 3). Layers containing opposite enantiomers are turned through 180° with respect to the *c* axis and shifted by a half translation (that is, the 2_1 screw axis occurs).

Previously, we found how the epitaxy could be prevented using special additives in the course of crystallization.[5] Studying **2** in this direction is in progress.

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